1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	10 DEC. 93	technical; 01JUN93 to 31MAY94

4. TITLE AND SUBTITLE

Polyimide/Inorganic Composite - Interpenetrating Polymer Network For Stable Second-Order Nonlinear Optics

5. FUNDING NUMBERS

C: N00014-90-J-1148

R&T Code: 4132016
Dr. JoAnn Milliken

6. AUTHOR(S)

S. Marturunkakul, J.-I Chen, L. Li, X. L. Jiang, R. J. Jeng, J. Kumar, S. K. Tripathy

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Massachusetts Lowell
Department of Chemistry
1 University Avenue
Lowell, MA 01854

8. PERFORMING ORGANIZATION REPORT NUMBER

1148-94-03

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research-Chemistry Division Code 1113
Department of the Navy
Arlington, Virginia 22217-5000

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Reproduction in whole or in part is permitted for any purpose of the United States Government.
This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 Words)*

A new class of IPN system has been prepared and investigated. This IPN system combines the polybismaleinimide network and the NLO-active phenoxysilicon network. The second-order NLO coefficients, d33, values of the samples range from 2.5 to 6.7 pm/V depending on the composition and the processing conditions. The temporal stability of the second-order nonlinearities for these samples at 110 °C varies from 47 to 88 % retention after 274 h.

14. SUBJECT TERMS

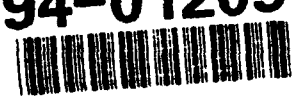
Interpenetrating polymer network.
Nonlinear optics.
Polybismaleinimide.

15. NUMBER OF PAGES

6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL



OFFICE OF NAVAL RESEARCH

GRANT N00014-90-J-1148

R&T Code 4132016

Scientific Officer: Dr. JoAnn Milliken

Technical Report No. 94-03

Polyimide/Inorganic Composite - Interpenetrating Polymer Network For Stable Second-Order Nonlinear Optics

by

S. Marturunkakul, J.-I Chen, L. Li, X. L. Jiang, R. J. Jeng, J. Kumar, S. K. Tripathy

Submitted to Materials Research Society

University of Massachusetts Lowell
Department of Chemistry
Lowell, Massachusetts

December 10, 1993

POLYIMIDE/INORGANIC COMPOSITE - INTERPENETRATING POLYMER NETWORK FOR STABLE SECOND-ORDER NONLINEAR OPTICS

SUTIYAO MARTURUNKAKUL*, JENG-I CHEN*, LIAN LI**, XIN LI JIANG**, RU JONG JENG*, JAYANT KUMAR**, AND SUKANT K. TRIPATHY*
Center for Advanced Materials, Departments of Chemistry* and Physics**, University of Massachusetts Lowell, Lowell, MA 01854, USA

ABSTRACT

A new class of IPN system has been prepared and investigated. This IPN system combines the polybismaleinimide network and the NLO-active phenoxysilicon network. The second-order NLO coefficients, d_{33}, values of the samples range from 2.5 to 6.7 pm/V depending on the composition and the processing conditions. The temporal stability of the second-order nonlinearities for these samples at 110 °C varies from 47 to 88 % retention after 274 h.

INTRODUCTION

There has been tremendous interest in the development of second-order nonlinear optical (NLO) polymeric materials for photonics applications [1]. A number of NLO polymers have been developed to exhibit large second-order NLO coefficients, d_{33}, comparable to those of the inorganic NLO materials which are currently in use in devices [2]. However, the major drawback of NLO polymers that prevents them from being employed in device applications is the decay of their electric field induced second-order optical nonlinearities. This decay is caused by the relaxation of the NLO chromophores from the induced acentric alignment to a random fashion. Numerous efforts have been made to minimize this decay through different approaches [3]. The search for a better material is still underway in order to make practical use of NLO polymers possible.

Recently, we have introduced a new approach using a concept of an interpenetrating polymer network (IPN) to prepare a second-order NLO polymer [4]. This IPN system, with the hybrid properties of a high glass transition temperature (T_g), an extensively cross-linked network, and permanent entanglements, exhibited excellent temporal stability at elevated temperatures. Since T_g is associated with the main-chain mobility, an increase of T_g results in enhanced temporal stability [5]. Polyimides have been used as high T_g matrices to enhance the stability in several guest/host systems [5a, 6]. Thus, the introduction of a cross-linkable high T_g polyimide into an IPN structure is expected to further advance the T_g of the system and boost the stability of the nonlinearity of the IPN.

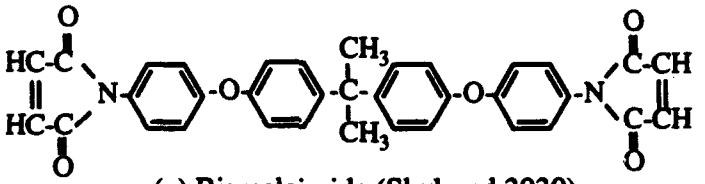
In this paper, we report an investigation of a new NLO-active IPN system combining a thermoset polyimide and an NLO-active inorganic network. The polyimide network based on bismaleimide is formed by an addition polymerization process. The NLO-active inorganic

network which is a phenoxysilicon polymer [7] is formed by sequential hydrolysis and condensation reactions via a sol-gel process. The formation of both networks are controlled to proceed simultaneously. The preparation of the IPN, the characterization of the thermal and optical properties, and the temporal stability of the optical nonlinearity are discussed.

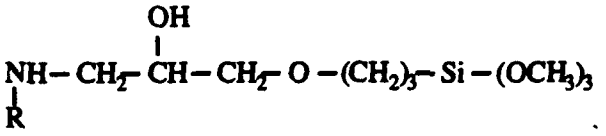
EXPERIMENTAL

Materials

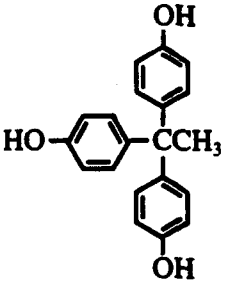
The NLO-active phenoxysilicon network is composed of an alkoxysilane dye (ASD-DO3) based on (3-glycidoxypropyl)trimethoxysilane and 4(4'-nitrophenylazo)aniline and the multifunctional phenoxyl molecule, 1,1,1-tris(4-hydroxyphenyl)ethane (THPE; Aldrich; Figure 1). The synthesis of the ASD-DO3 is described elsewhere [8]. The polyimide network is prepared from 2,2-bis[4-(4-maleimido phenoxy)phenyl]propane monomer (Skybond 3030; Monsanto Chemical Co.; Figure 1). The monomer was used as received.



(a) Bismaleimide (Skybond 3030)



(b) ASD



(c) THPE

Figure 1. Chemical structures of (a) Bismaleimide, (b) ASD-DO3, and (c) THPE.

Sample preparation

To prepare thin film samples, 0.1 g of ASD-DO3 and 0.07 g of THPE (molar ratio = 1.0:1.1) was dissolved in 1 mL of dimethylformamide (DMF) containing 24 mg of water and 24 mg of N,N-dimethybenzylamine. The presence of water and base catalyst is to aid in the hydrolysis of the alkoxysilane. The solution was stirred for 4 h at room temperature. A second solution was prepared by adding 0.17 g of Skybond 3030 with 1% by weight of 2-ethyl-4-methylimidazole in 1 mL of DMF. This solution was stirred for 30 min in a 95 °C oil bath to form prepolymer prior to curing. The number average molecular weight of the prepolymer was determined to be 5400 g/mole by gel permeation chromatography using polystyrenes standards.

Both solutions were mixed together and the resulting solution contained a weight ratio of 1:1 bismaleimide to ASD-DO3/THPE. Two other solutions were prepared in a similar manner with weight ratios of 0:1 and 1:2 bismaleimide to ASD-DO3/THPE. The solutions were filtered through 0.2 μm membranes before they were spin-coated onto transparent microscope slides at a spinning rate of 800 rpm to form optical quality thin films. They were also spin-coated on fully frosted microscope slides and KBr plates for the ellipsometric and FTIR measurements, respectively.

The corona poling technique [9] was employed to align the NLO chromophores. The corona field was applied as the temperature was raised to 80 °C. The temperature was then increased to 220 °C with the corona field on. The corona current was maintained at 2 μA with a potential of 4 kV while the poling temperature was kept at 220 °C for 60 min. The formation of the networks and the molecular alignment for the poled order proceeded simultaneously during this period. The sample was then cooled down slowly to room temperature before the corona field was turned off. In the case of 1:1 composition, the sample was also cured at 240 °C for the sake of comparison. The sample compositions and the processing temperatures are illustrated in Table 1. The second-order NLO properties of the poled IPN samples were measured by second harmonic (SH) generation from 1.064 μm laser radiation. The relaxation behavior of the second-order NLO properties was studied by monitoring the decay of the SH intensity as a function of time at 110 °C after poling and curing.

Table 1. Sample compositions and processing conditions.

Sample ID	Composition (weight ratio)		Processing Condition
	Bismaleimide	ASD/THPE	
A	1	1	1 h @ 240 °C
B	1	1	1 h @ 220 °C
C	1	2	1 h @ 220 °C
D†	0	1	1 h @ 220 °C

† Phenoxysilicon polymer

RESULT AND DISCUSSION

Figure 2 shows the IR spectra for sample B before and after curing. The formation of the polybismaleinimide network through a free radical addition reaction is confirmed by the reduction of C=C absorption at 1662 cm^{-1}, and the reduction of 691 cm^{-1} band that corresponds to cis C-H wagging frequency [10]. The formation of the phenoxysilicon network via a sol-gel process is suggested by the decrease of hydroxyl absorption peak (3387 cm^{-1}), and the emergence of a new peak at 937 cm^{-1} which corresponds to the phenoxysilicon absorption [10]. The crosslinking reactions can also be observed from the IR spectra for other samples before and after curing.

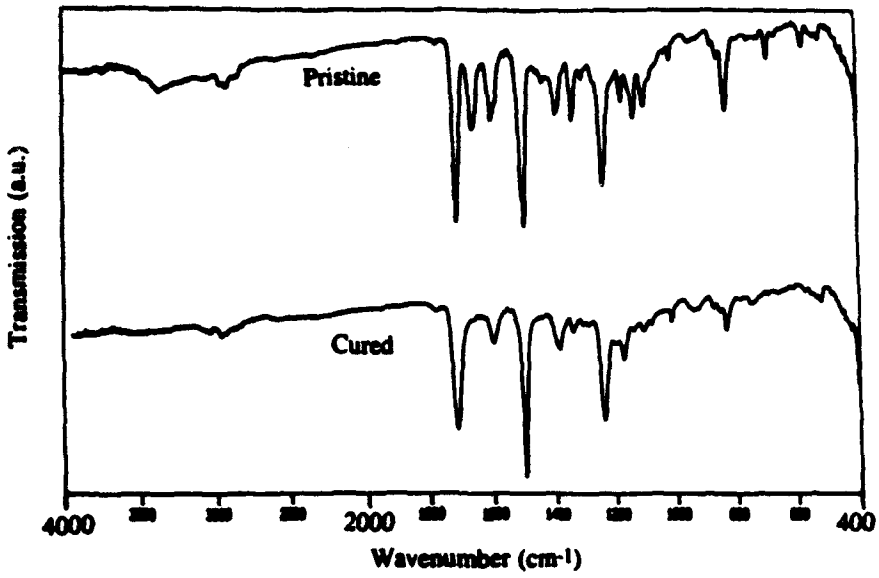


Figure 2. IR spectra for the IPN sample B: (top) pristine, (bottom) cured 1 h at 220 °C.

The T_g of the polybismaleinimide is reported to be higher than 300 °C when the initial curing is done at 260 °C and post curing at 315 °C [11]. The T_gs of all samples in this study, however, could not be observed from the DSC scans despite several attempts at both the scanning rates of 10 and 20 °C/min. This could be a result of suppression of the T_g by extensive cross-links in the IPN. The poled and cured samples exhibit excellent optical quality. No phase separation was observed under the optical microscope. Further investigations on the phase behavior using transmission electron microscopy and the optical loss measurements of these samples are underway.

The optical properties of the poled and cured samples are summarized in Table 2. The lower d_{33} values of sample A compared with that of sample B are caused by a lower order parameter for the chromophores in the former. The high poling temperature can cause large thermal fluctuation (kT) and ionic conductivity which can fight against the aligning torque of the poling field [12]. The d_{33} values of samples increase from samples B to D, respectively. This is expected as the NLO chromophore concentrations increased accordingly.

Table 2. Optical properties of the poled and cured samples.

Sample ID	Refractive indices		d_{33} (pm/V)†	% d_{33} retention††
	at 0.532 μm	at 1.0 μm		
A	1.600	1.578	2.5	74
B	1.657	1.611	3.2	47
C	1.603	1.578	6.7	88
D	1.744	1.635	7.6	71

† at 1.064 μm, the values were corrected for the absorption

†† after thermal treatment at 110 °C for 274 h.

The temporal stability of the samples at 110 °C is illustrated in Figure 3. The dramatic superiority in the stability of sample A compared to of sample B is due to the higher processing temperature of the former. This results in a more extensive cross-linked network in sample A relative to sample B. The superior stability of the IPN sample C than that of the single component phenoxysilicon polymer (sample D) suggests that the IPN architecture plays an important role in the enhancement of the stability for the NLO properties. It is interesting to observe that the temporal stability is also affected by the compositions of the IPN samples as compared between samples B and C. The temporal stability decreases when the portion of the bismaleimide in the IPN structures is increased in sample B. Since the decay of the nonlinearity results from the relaxation of poled NLO chromophores, it is suggested that the chain mobility and local free volume may have varied as the samples were prepared in different compositions. For example, with a limited extent of reaction at 220 °C [13], the remaining unreacted maleimide rings at the polymer chain ends could have created a large free volume allowing the dipolar relaxation to occur. The physical properties of these composites varied with their chemical compositions leading to a change in the decay behavior of the poled order.

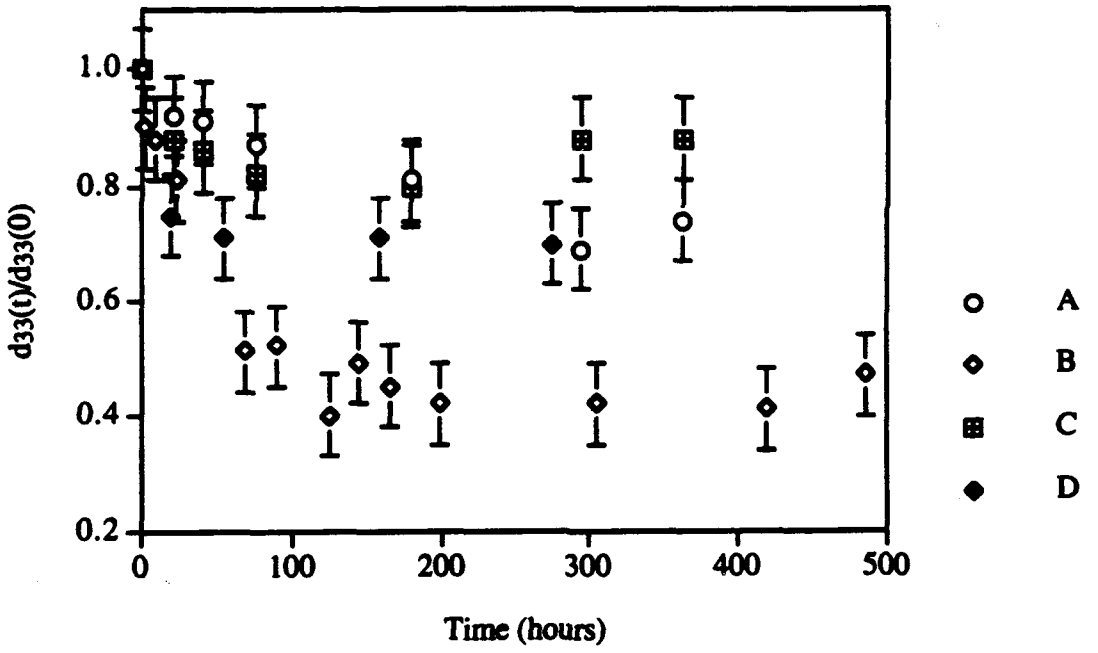


Figure 3. The temporal stability of the samples subjected to thermal treatment at 110 °C.

CONCLUSION

A new class of NLO-active IPN based on the polybismaleinimide and phenoxysilicon networks was prepared. It was found that the temporal stability was enhanced as the processing temperatures increased from 220 to 240 °C. The temporal stability of the samples was affected

by the molecular compositions. Further improvements can be achieved by the incorporation of NLO chromophores in the polyimide network, and the optimization of the compositions as well as the processing conditions.

ACKNOWLEDGMENT

Partial funding from ONR is gratefully acknowledged.

REFERENCES

1. (a) R.J. Twieg and K. Jain in *Nonlinear Optical Properties of Organic and Polymeric Materials*, edited by D.J. Williams (ACS Symposium Series 233, American Chemical Society, Washington, DC, 1982) p 57. (b) *Nonlinear Optical Properties of Organic Molecules and Crystal*, edited by D.S. Chemla and J. Zyss (Academic Press, New York, 1987) vol. 1 and 2.
2. (a) P.N. Prasad and D.J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, (John Wiley & Sons, New York, 1991) pp.59-260. (b) D.F. Eaton, Science **253**, 281 (1991).
3. (a) M. Eich, B. Reck, D.Y. Yoon, C.G. Willson, and G.C. Bjorklund, J. Appl. Phys. **66**, 3241 (1989). (b) B.K. Mandal, J. Kumar, J.C. Huang, and S.K. Tripathy, Makromol. Chem., Rapid Commun. **12**, 63 (1991). (c) R.J. Jeng, Y.M. Chen, J. Kumar, and S.K. Tripathy, J. Macromol. Science-Pure Appl. Chem. **A29**, 1115 (1992). (d) Y. Shi, P.M. Ranon, W.H. Steier, C. Xu, B. Wu, and L.R. Dalton, Appi. Phys. Lett. **63**, 16 (1993).
4. (a) S. Marturunkakul, J.I. Chen, L. Li, R.J. Jeng, J. Kumar, and S.K. Tripathy, Chem. Mater. **5**, 592 (1993). (b) S. Marturunkakul, J. Kumar, and S.K. Tripathy, Proc. Am. Chem. Soc., Div. Polym. Mat.: Sci. & Eng. **69**, 436 (1993). (c) J.I. Chen, S. Marturunkakul, L. Li, R.J. Jeng, J. Kumar, and S.K. Tripathy, Macromolecules, in press.
5. (a) M. Stähelin, D.M. Burland, M. Ebert, R.D. Miller, B.A. Smith, R.J. Twieg, W. Volksen, and C.A. Walsh, Appl. Phys. Lett. **61**, 1626 (1992). (b) J. Kim, J.L. Plawsky, E.V. Wagenen, and G.M. Korenowski, Chem. Mater. **5**, 1118 (1993). (c) D. Jungbauer, B. Reck, R. Twieg, D.Y. Yoon, C.G. Willson, and J.D. Swalen, Appl. Phys. Lett. **56**, 2610 (1990).
6. (a) J.W. Wu, J.F. Valley, S. Ermer, E.S. Binkley, J.T. Kenney, G.F. Lipscomb, and R. Lytel, Appl. Phys. Lett. **58**, 225 (1991). (b) M.A. Hubbard, T.J. Mark, W. Lin, and G.K. Wong, Chem. Mat. **4**, 965 (1992).
7. R.J. Jeng, Y.M. Chen, J.I. Chen, J. Kumar, and S.K. Tripathy, Macromolecules **26**, 2530 (1993).
8. R.J. Jeng, Y.M. Chen, A.K. Jain, J. Kumar, and S.K. Tripathy, Chem. Mater. **4**, 972 (1992).
9. (a) K.D. Singer, J.E. Sohn, and S.J. Lalama, Appl. Phys. Lett. **49**, 248 (1986). (b) M.A. Mortazavi, A. Knoesen, S.T. Kowel, B.G. Higgins, and A. Dienes, J. Opt. Soc. Am. B, **6**, 733 (1989). (c) R.J. Jeng, Y.M. Chen, A.K. Jain, S.K. Tripathy, and J. Kumar, Optics Commun. **89**, 212 (1992).
10. (a) R.M. Silverstein, G.C. Bassler, and T.C. Morrill, *Spectrometric Identification of Organic Compounds*, (John Wiley and Sons, New York, 1981) pp. 95-125. (b) D. Lin-Vien, N.B. Colthup, W.G. Fateley, and J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, (Academic Press, San Diego, 1991) pp. 10-233.
11. Monsanto Chemical Co. Material data sheet for Skybond 3030. Publication no. 8225, 1993.
12. G.A. Lindsay, R.A. Henry, J.M. Hoover, A. Knoesen, and M.A. Mortazavi, Macromolecules **25**, 4888 (1992).
13. A.C. Lind and C.G. Fry, Polym. Mater. Sci. Eng. **59**, 466 (1988).

Office of Naval Research (1)
Chemistry Division, Code 313
800 North Quincy Street
Arlington, VA 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, DC 20375-5000

Dr. Robert Green, Dir. (1)
Chemistry Division, Code 385
Naval Weapons Center
Weapons Division
China Lake, CA 93555-6001

Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Dr. Bernard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, IN 47522-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Elek Lindner (1)
Naval Command,
Control and Ocean Surveillance Center
RDT&E Division
San Diego, CA 92152-5000